A study of the glass transition of amylopectin–sugar mixtures

M. T. Kalichevsky, E. M. Jaroszkiewicz and J. M. V. Blanshard*
Department of Applied Biochemistry and Food Science, Nottingham University, School of Agriculture, Sutton Bonington, Loughborough LE12 5RD, UK
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Amylopectin–sugar mixtures in the ratio of 10:1 have been studied using fructose, glucose, sucrose and xylose. Samples of amylopectin containing glucose in the ratio of 5:1 and fructose in the ratio of 2:1 (amylopectin–sugar) were also prepared. The glass transition as a function of water content was studied using d.m.t.a., d.s.c., pulsed n.m.r. and a three-point bend test. Small amounts of sugar were found to reduce the glass transition temperature of starch in accordance with or in excess of the predictions of a Couchman–Karasz equation. For the sample containing the greatest amount of sugar, less plasticization than predicted was observed; this appeared to be due to a substantial degree of phase separation.

(Keywords: glass transition; free volume; amylopectin)

INTRODUCTION

A study of the glass transition region of amylopectin from waxy maize starch as a function of water content has already been carried out, using n.m.r. d.s.c., d.m.t.a. and an Instron texturometer[1]. This work has now been extended to investigate the effect of sugars (glucose, sucrose, fructose and xylose) on the glass transition temperature (T_g) of amylopectin–sugar systems in the presence of water. An understanding of such starch–sugar mixtures would be a step towards understanding real food systems such as baked products, which are heterogeneous, multicomponent systems.

The glass transition has been invoked by Levine and Slade[2] to explain the increase in the gelatinization temperature of starch which is widely observed for 1:1:1 starch–sugar–water systems when compared with 1:1 starch–water systems. They argue that sugar has an antiplasticizing effect relative to water, increasing the T_g of the water-plasticized amorphous regions of amylopectin. A similar argument is used to explain the decreased rate of starch retrogradation (recrystallization) observed in the presence of sugars of similar compositions. Even though the experimental temperature (25°C) is 60–100°C above the theoretical T_g of such systems, it is thought that the kinetics of retrogradation are still very dependent on the ΔT above T_g. If the underlying T_g is increased, the ΔT will be decreased and hence the extent and rate of retrogradation will be reduced. Staling is thought to be largely due to starch retrogradation[3]; thus an understanding of these phenomena would be of practical importance.

It should be pointed out that the description of sugars as antiplasticizing agents may be misleading. In the above studies sugars are compared to water as a plasticizer but they would be expected to be less efficient plasticizers due to their higher molecular weight and higher T_g relative to water. It is misleading to compare a 1:1 starch–water mixture, with a 1:1:1 starch–sugar–water mixture, as the resulting water content is decreased from 50% of the total weight to 33.3% of the total weight. It will be shown here that in samples containing the same weight fraction of water, sugars do in fact have a plasticizing effect on the T_g of amylopectin as would be expected due to their lower molecular weight and lower T_g when compared with starch. This type of behaviour has recently been observed by Ollett *et al.*[4] for wheat starch and glucose.

In this study the observed glass transition is studied by a variety of techniques and the applicability of various theories is tested.

THEORIES OF PLASTICIZATION APPLIED TO AMYLOPECTIN

There are several equations (empirical and theoretical) relating the glass transition of mixtures to the properties of the components. There are two main theoretical approaches which are rather crude[5] but have proved useful. These are free volume theory (assuming the glassy state is an iso-free volume state) and thermodynamic theory (assuming continuity of the excess entropy of mixing at T_g).

Free volume theory

At the glass transition there is a change in the volume expansion coefficient ($\Delta\alpha$). This is thought to be due to the attainment of a critical free volume and the glassy state is considered as an iso-free volume state[6]. An extension of the free volume theory[7] has been used to model the unusual composition dependence of T_g of some miscible polymer blends[8].

The applicability of the free volume approach may be limited as the dependence of free volume on molecular weight, intermolecular forces, chain flexibility, chain

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* To whom correspondence should be addressed

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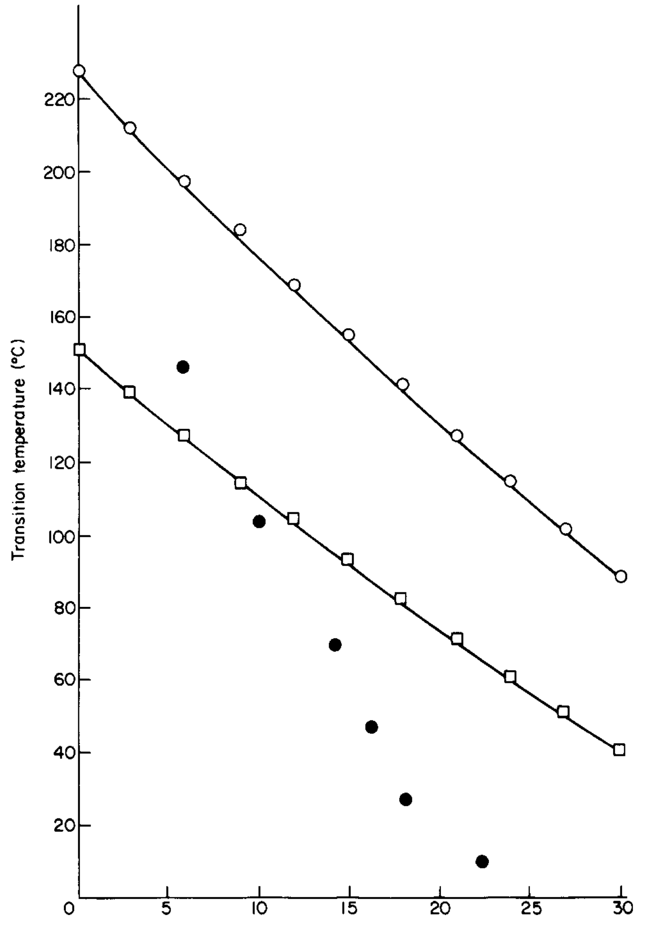

Figure 1 Free volume theories [$T_g = 500$ K (227°C) (○); $T_g = 424$ K (151°C) (□)] compared with experimental d.s.c. data on amylopectin (●)

geometry and structural details such as the bulkiness of side groups is not taken into account. In the case of biopolymers such as those studied here, intermolecular interactions and hydrogen bonding may play a significant role in plasticization behaviour[9]. The free volume approach therefore, may be useful in some cases.

An equation describing the effect of a diluent on T_g was derived using a free volume approach by Bueche[10]. This equation, as quoted below, was applied to amylopectin:

$$T_g = \frac{\Delta\alpha_p V_p T_{g_p} + \Delta\alpha_d (1 - V_p) T_{g_d}}{\Delta\alpha_p V_p + \Delta\alpha_d (1 - V_p)} \qquad (1)$$

The subscripts p and d refer to the polymer and diluent, respectively. $\Delta\alpha$ is the difference in the volume expansion coefficients above (rubbery) and below (glassy state) T_g ($\alpha_r - \alpha_g$). Typically $\Delta\alpha_p = 4.8 \times 10^{-4}\,\mathrm{K}^{-1}$ and $\Delta\alpha_d = 1 \times 10^{-3}\,\mathrm{K}^{-1}$. V is the volume fraction, obtained using the following density values: $\rho_{\mathrm{starch}} = 1.517\,\mathrm{g\,cm^{-3}}$, $\rho_{\mathrm{water}} = 1\,\mathrm{g\,cm^{-3}}$ and $\rho_{\mathrm{glucose}} = 1.523\,\mathrm{g\,cm^{-3}}$, with T_{g_d} (water) = 134 K (−139°C).

Assuming additivity of free volume on mixing, low molecular weight diluents will have a plasticizing (T_g reducing) effect as they have a higher free volume than polymers. Increased free volume results in increased polymer segmental mobility. The plasticizing effect of a diluent decreases linearly with increasing diluent molecular weight and T_g, albeit with some scatter[2].

Two different T_g values for dry starch in the literature[11,12] were used to obtain two theoretical curves from equation (1), using the typical values for $\Delta\alpha_d$ and $\Delta\alpha_p$ above. A comparison with experimental d.s.c. data for amylopectin (*Figure 1*) suggests that the correct dry T_g for amylopectin is higher than the van den Berg values[12] (151°C) and that water has a greater plasticizing effect than predicted by this theory. Similar results are obtained when sugar is added to starch, in equation (1), and then the new T_g put into equation (1) again, assuming the same value for $\Delta\alpha_p$, i.e. the plasticizing effect of sugar and water are both underestimated by this method.

The question is then raised whether the values used for $\Delta\alpha_p$ and $\Delta\alpha_d$ are appropriate. The value used for $\Delta\alpha_p$ of starch ($4.8 \times 10^{-4}\,\mathrm{K}^{-1}$) seems to be of the right order of magnitude as values for polymers are generally between $2 \times 10^{-4}\,\mathrm{K}^{-1}$ and $5 \times 10^{-4}\,\mathrm{K}^{-1}$ and elastin was found to have a value of 2.9×10^{-4} at 14% water[13]. The value used for $\Delta\alpha_d$ is more uncertain, however. In the case of glucose[7] $\Delta\alpha_d = 2.8 \times 10^{-4}\,\mathrm{K}^{-1}$ and for (liquid) water $\alpha_L = 2.07 \times 10^{-4}\,\mathrm{K}^{-1}$, so $\Delta\alpha_d$ ($= \alpha_L - \alpha_g$) cannot be larger than this. In both cases this is much smaller than the value of $1 \times 10^{-3}\,\mathrm{K}^{-1}$ used. Smaller (more correct) values of $\Delta\alpha_d$ would further reduce the predicted plasticizing action. It has been shown[14] that the free volume equation works well when polymer–diluent interactions are weak but when they are strong, free volume theory fails and an entropy model is more successful. Thus interactions occurring in starch–sugar–water systems may cause the failure of the Bueche equation.

Couchman–Karasz classical thermodynamic approach

The Couchman–Karasz[15] and Couchman[16] treatment of the composition dependence of T_g assumes continuity of the configurational entropy at T_g. It also assumes intimate miscibility and the absence of crystallinity or crosslinking, although subsequent papers have examined these effects[17]. The most general form of the equation is:

$$\ln T_g = \frac{W_1 \Delta C_{p_1} \ln T_{g_1} + W_2 \Delta C_{p_2} \ln T_{g_2}}{W_1 \Delta C_{p_1} + W_2 \Delta C_{p_2}} \qquad (2)$$

where subscripts 1 and 2 refer to the two components. W_1 is the weight fraction of component 1 and ΔC_p is the difference in specific heats between the liquid and glass states at T_g. This equation assumes that ΔC_p is independent of temperature.

When equation (2) is applied to amylopectin and water using the extrapolated values of Orford *et al.*[11] for ΔC_p ($0.47\,\mathrm{J\,g^{-1}\,K^{-1}}$) and T_g (500 K, 227°C) of starch [$1.94\,\mathrm{J\,g^{-1}\,K^{-1}}$ and 134 K (−139°C) for water], the theoretical T_g falls well below the observed T_g (*Figure 2*), i.e. equation (2) results in an overestimate of the T_g depression. This is also observed for three-component systems containing sugar.

This may be because the assumption that ΔC_p is independent of temperature is not valid, as observed by ten Brinke *et al.*[18]; this would be more important in polymer–plasticizer systems where the T_gs are far apart. If it is assumed that ΔC_p is inversely proportional to temperature then the following equation may be derived[18]:

$$T_g = \frac{W_1 \Delta C_{p_1} T_{g_1} + W_2 \Delta C_{p_2} T_{g_2}}{W_1 \Delta C_{p_1} + W_2 \Delta C_{p_2}} \qquad (3)$$

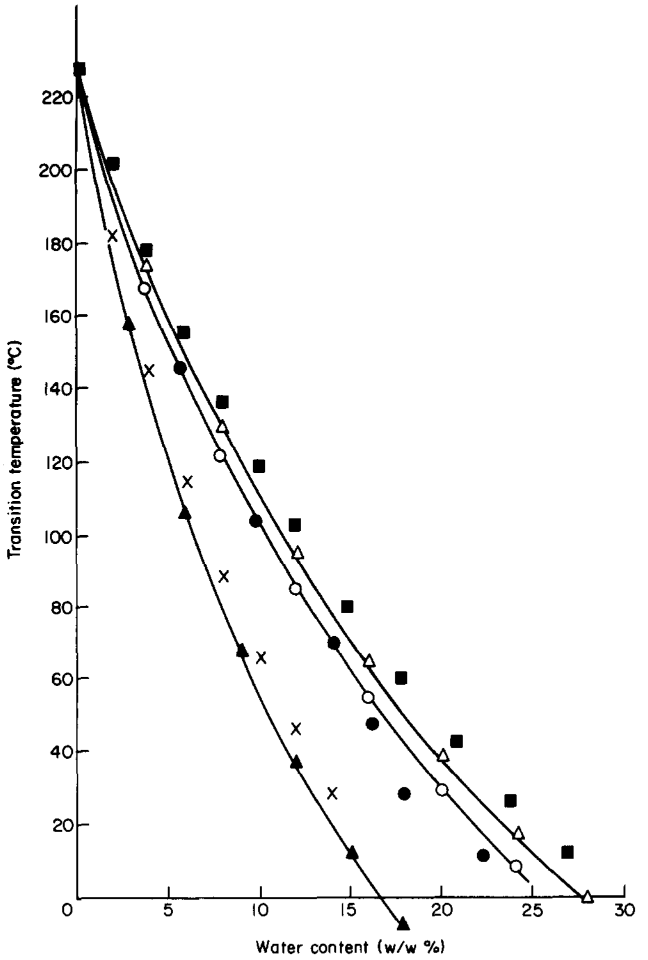

Figure 2 Couchman–Karasz classical thermodynamic theoretical equations and derived equations (see text) compared with experimental d.s.c. data (●). Equation (2) (▲); equation (3) ($\Delta C_p = 0.47\,\mathrm{J\,g^{-1}\,K^{-1}}$) (△); equation (3) ($\Delta C_p = 0.425\,\mathrm{J\,g^{-1}\,K^{-1}}$) (○); equation (4) (■); equation (5) (×)

Equation (3) has also been previously derived using classical thermodynamic theory[15], but that derivation suggested a very restricted applicability. When equation (3) is applied to the amylopectin–water system a much better fit to the data is obtained. A better fit still was obtained using a value of $0.425\,\mathrm{J\,g^{-1}\,K^{-1}}$ for ΔC_p. (The value of $0.47\,\mathrm{J\,g^{-1}\,K^{-1}}$ was an asymptotic value derived from ΔC_p values for malto-oligosaccharides[11], and therefore may not be very accurate). Our experimental values of ΔC_p for amylopectin–water mixtures were somewhat smaller than this and were very scattered. Additionally it is uncertain what effect water has on ΔC_p. Thus we decided to use a value of $0.425\,\mathrm{J\,g^{-1}\,K^{-1}}$ in subsequent calculations.

Other previously empirical equations may be derived from the Couchman–Karasz equation, equation (3), e.g. the inverse rule of mixtures may be derived by assuming that $\Delta C_{p_1} T_{g_1}$ is a constant.

$$\frac{1}{T_g} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}} \tag{4}$$

When this is applied to amylopectin or amylopectin–sugar mixtures the predicted plasticization is less than observed (*Figure 2*), indicating that this is not a very good assumption for these systems. (The T_g and ΔC_p values of sugars were obtained from Orford *et al.*[19].)

Fried *et al.*[20] derived a form of equation (2) which avoids the use of ΔC_p, by assuming that $\Delta C_p T_g$ is a constant:

$$\ln\left(\frac{T_g}{T_{g_1}}\right) = \frac{W_2 \ln (T_{g_2}/T_{g_1})}{W_1 (T_{g_2}/T_{g_1}) + W_2} \tag{5}$$

As with equation (2), this equation overestimates the plasticizing effect of water. These theoretical curves are plotted with experimental (d.s.c.) results for amylopectin in *Figure 2*.

Equation (3) appears to give the best fit for $T_{g_{\mathrm{d.s.c.}}}$ (at $10\,\mathrm{K\,min^{-1}}$) of amylopectin and water[1]. This equation has been successfully used to predict T_g of polymer–diluent systems[21]. In the case of sugars and starch oligomers, equation (3) underestimated the T_g depression of sugars by water[11] and of sugar mixtures[19].

There are various literature values[11,19,22] for ΔC_p of sugars. The values for ΔC_p and T_g of fructose from Orford *et al.*[19] gave the best fit to d.s.c. (at $10\,\mathrm{K\,min^{-1}}$) fructose–water data obtained in this laboratory[23], using equation (3). As a result, values of Orford *et al.*[19] for other sugars were also used, without further investigation. These were obtained by d.s.c. at a heating rate of $10°\mathrm{C\,min^{-1}}$, which is the same heating rate used in our d.s.c. experiments. The values of T_g and ΔC_p used for the sugars are given in *Table 1*. In the case of a three-component system two methods were used to obtain a theoretical T_g. 'Method 1' involved applying equation (3) to starch and sugar in the ratio used to obtain a T_g of the dry mixture, this value is put into the equation again with water as a second component. A value of $0.425\,\mathrm{J\,g^{-1}\,K^{-1}}$ was used as ΔC_p for the starch–sugar mixture. This assumes that ΔC_p (starch and sugar) = ΔC_p (starch alone). 'Method 2' involves expanding equation (3) to take account of the extra component:

$$T_g = \frac{W_1 \Delta C_{p_1} T_{g_1} + W_2 \Delta C_{p_2} T_{g_2} + W_3 \Delta C_{p_3} T_{g_3}}{W_1 \Delta C_{p_1} + W_2 \Delta C_{p_2} + W_3 \Delta C_{p_3}} \tag{6}$$

where subscripts 1, 2 and 3 refer to water, amylopectin and sugar, respectively.

The two-component approach (method 1) described above was found to give a better fit to the data for starch–sugar–water mixtures. As a result this curve is plotted with each set of d.s.c. data in the results.

Effect of interactions on T$_g$

Polysaccharides, sugars and water are all very hydrophilic and may be expected to associate by means of hydrogen bonding. In the case of polymer blends, interactions between the components have resulted in a T_g higher than that of either component[24]. Increasing the number of hydrophilic groups has been found[25–28] to result in an increased T_g, and the effect of hydrogen bonding plasticizers, especially water, may be enhanced with increasing polymer hydrophilicity[27,29]. However, ten Brinke *et al.*[18] and Ellis *et al.*[30] believe that if factors

Table 1 Values of T_g and C_p for the sugars

	T_g [K (°C)]	ΔC_p ($\mathrm{J\,g^{-1}\,K^{-1}}$)
Glucose	311 (38)	0.88
Fructose	280 (7)	0.83
Sucrose	343 (70)	0.76
Xylose	286 (13)	0.95

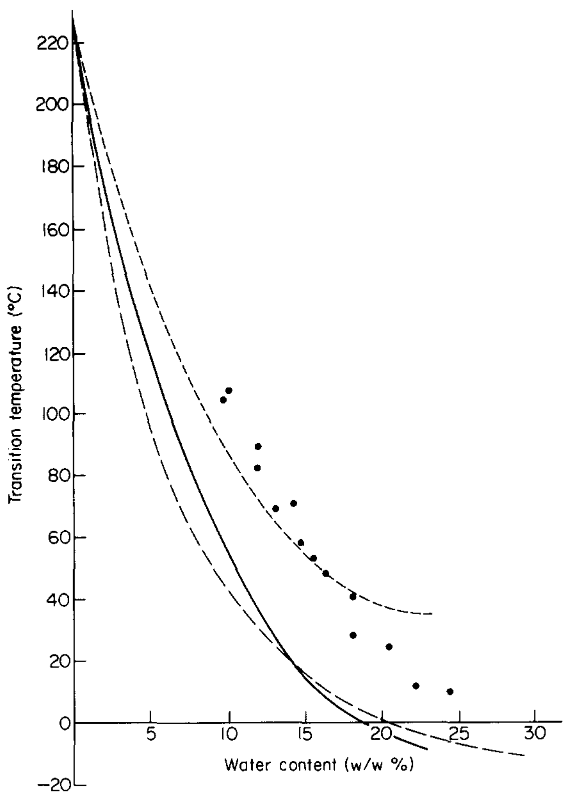

Figure 3 Equations taking account of interactions: Kwei equation (— —) and Carter–Kibler equation [$\Delta C_p = 0.47$ (- - - -) and $0.38\,\mathrm{J\,g^{-1}\,K^{-1}}$ (——)] compared with $T_{g_{d.s.c.}}$ for amylopectin

such as phase separation and crystallinity are taken into account, it is not necessary to resort to concepts of specific interactions and data may be fitted to the Couchman–Karasz equation.

The Gordon–Taylor equation is an empirical equation for predicting the T_g of mixtures from the T_gs of the components:

$$T_g = \frac{W_1 T_{g_1} + K W_2 T_{g_2}}{W_1 + K W_2} \tag{7}$$

However this equation is equivalent to the Bueche equation, equation (1) if:

$$K = \rho_1 \Delta\alpha_2 / \rho_2 \Delta\alpha_1 \tag{8}$$

or K equals the change in expansion coefficients if W equals the volume fraction. Equation (7) is equivalent to the Couchman–Karasz equation, equation (3), if:

$$K = \Delta C_{p_2} / \Delta C_{p_1} \tag{9}$$

The Kwei equation[31] extends the Gordon–Taylor equation by a quadratic term and has been used in cases where strong interactions cause the Gordon–Taylor equation to fail:

$$T_g = \frac{W_1 T_{g_1} + K W_2 T_{g_2}}{W_1 + K W_2} + q W_1 W_2 \tag{10}$$

This equation was first applied to mixtures of poly(methyl methacrylate) with Novolac resins[31] and has more recently been applied to wood and wood components, plasticized by water[32]. Originally the value of q was expected to be positive and to be related to the number of interactions or hydrogen bonds between components[31], but negative values of q have since been obtained, which are thought to arise from electrical or steric/polarizability effects[33]. The sign of q may depend on the balance between self-association and association between different components, and the dependence of this on composition[34]. The value of q has been found to decrease with decreasing phenolic hydroxyl content in lignin[32] which corresponds to the idea that q is proportional to the degree of hydrogen bonding. Negative values of q obtained for nylon blends have been attributed to variations in flexibility[35] (or steric hindrance).

An attempt was made to check the Kwei equation against our data for amylopectin. First the values of K and q obtained for hemicellulose[32] (13 and 355, respectively) were plotted using 500 K as T_{g_1}. The curve obtained (*Figure 3*) greatly overestimated the plasticizing effect of water on amylopectin, so these values are not suitable for amylopectin.

An extended third-order virial equation has been used to determine the effect of interactions on T_g of compatible polymer blends[36]. A plot of $(T_g - T_{g_1})/(T_{g_2} - T_{g_1})W_{2c}$ against W_{2c} [where $W_{2c} = KW_2/(W_1 + KW_2)$] gives a straight horizontal line about unity if the Gordon–Taylor equation holds. If the Kwei equation holds, a straight line with a slope from which q may be determined is obtained. In more complex systems a curve is obtained. Using the value of K effectively used in the Couchman–Karasz equation [0.219, using equation (9)] the y values are within 0.03 of 1 and show no significant dependence on water content, indicating that the Gordon–Taylor equation gives a good fit to the data. This is further shown using the linearized form of the Gordon–Taylor equation[37].

A plot of $\log[(T_g - T_{g_1})/(T_{g_2} - T_g)]$ against $\log[W_2/(1 - W_2)]$ must give a straight line of slope 1 and intercept $\log K$. When all the d.s.c. data for amylopectin are plotted in this way (*Figure 4*, using subscript 1 = water and subscript 2 = amylopectin) a straight line of slope 1 is obtained and the intercept gives a K value of 0.195. [The value used in the Couchman–Karasz equation, as calculated using equation (8), is 0.219].

Carter and Kibler[38] devised a configurational entropy model for polymer–diluent systems with highly polar groups, assuming localization of the plasticizer on the polar groups of the polymer. Their equation, equation (11), has been successfully applied to wet epoxy resins[14,38]:

$$T_{g_f} = T_{g_0}\{1 - [R/(M_s \Delta C_p)]\,y(r)\} \tag{11}$$

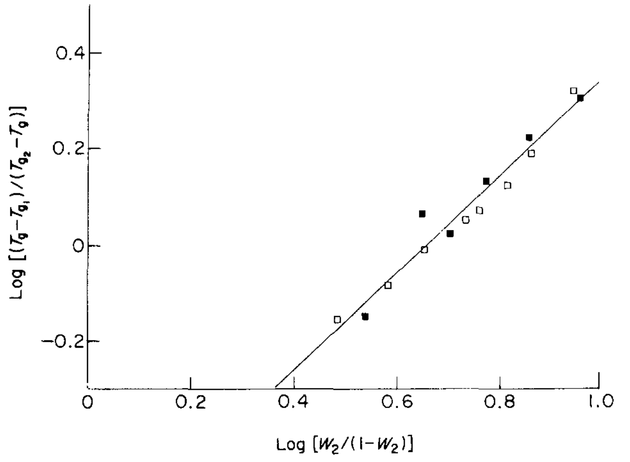

Figure 4 Gordon–Taylor fit to $T_{g_{d.s.c.}}$ for amylopectin–water mixture

where

$$y(r) = r\ln(1/r) + (1-r)\ln[1/(1-r)] \quad (12)$$

R is the universal gas constant and r is the ratio of the number of water molecules to hydrogen bond sites. This may be calculated from the effective formula weight per hydrogen bond site (M_s) and the formula weight of water ($M_w = 18\,\mathrm{g\,mol^{-1}}$):

$$r = (M_s/M_w)f \quad (13)$$

where f is the weight fraction of water.

Equation (11) was plotted assuming that all oxygens are potential hydrogen bond sites, and yielded a value of 1.8 for M_s/M_w of amylopectin and water. This equation predicts a pronounced reduction in the T_g dependence on plasticizer content at higher plasticizer contents, which is frequently observed in these systems. However the observed reduction in plasticization could be due to phase separation rather than interactions[18]. The curve obtained was found to be very sensitive to the value of C_p used. The Orford *et al.*[11] value ($0.47\,\mathrm{J\,g^{-1}\,K^{-1}}$) and especially the best fit value to the Gordon–Taylor equation [$0.38\,\mathrm{J\,g^{-1}\,K^{-1}}$, using equation (9)] result in an overestimate of the plasticizing effect of water at low water contents. At higher water contents the Orford *et al.* value gives a plateau T_g value of 40°C, which is obviously too high (*Figure 3*). Thus the Carter–Kibler equation does not fit our data at all well.

The Kaelble equation was successfully used[39] to calculate the T_g of cellulose and other wood components with various plasticizers. It is in fact an equation of the Gordon–Taylor form [equation (7)] with $K = h_2/h_1$, where $h = (2\delta^2\gamma)/(RT_g)$, δ is the solubility parameter, γ is the molar volume and subscripts 1 and 2 refer to the polymer and diluent, respectively (the opposite to that used above). Using the values obtained[39] for cellulose gives a value of $K = 0.47$. The best fit to the Gordon–Taylor equation gave a value of 5.1. Therefore it is apparent that a value of 0.47 will grossly underestimate the plasticizing effect of water on starch.

Summary

The best fit to $T_{g_{\mathrm{d.s.c.}}}$ of amylopectin–water mixtures[1] was found to be given by the Couchman–Karasz equation, equation (3). This equation is easily extended to take account of multicomponent systems. Use of equations attempting to take account of interactions does not appear to be necessary or applicable to this system. The best fit to the $T_{g_{\mathrm{d.s.c.}}}$ of the three-component systems studied here was obtained using equation (3) (as described above and shown in the Discussion). These curves are plotted with the d.s.c. data.

EXPERIMENTAL

Sample preparation

Amylopectin was supplied either as waxy maize starch or in the pregelatinized form by National Starch and Chemical Corp., Manchester, UK. The waxy maize starch was gelatinized as a 50% w/w water mixture in a boiling water bath. Sugar–starch mixtures were also prepared by this method using a sugar solution of the appropriate concentration in place of water. Alternatively, solutions of sugars (glucose, fructose, sucrose or xylose) were ground in liquid nitrogen and pregelatinized waxy maize starch was then added and mixed with the powdered solutions. The nitrogen was allowed to evaporate. The samples were subsequently pressed under a pressure of 3.1×10^8 Pa at a temperature of 90–100°C for 5–10 min and hydrated over various saturated salt solutions of specified relative humidity (r.h.). The water content was established by oven drying at 105°C to constant weight. X-ray diffraction was used to test for sugar or starch recrystallization. No sugar recrystallization was observed in the samples used.

N.m.r. measurements

T_2 relaxation measurements were carried out using a 60 MHz home-built n.m.r. spectrometer constructed in this laboratory with a Varian 1.4 T magnet. Samples were placed in a 7 mm o.d. tube. A 90° pulse of 8 μs length was applied to the system; the repetition rate was 1 s; 16 transients were co-added. The T_2 was measured straight from the free induction decay (f.i.d.), which consisted of 1024 points. The data were analysed by a BBC microcomputer, interfaced with an n.m.r. spectrometer. The typical decay obtained from samples after the application of the 90° pulse consisted of two components. The first one (T_{2s}) with a T_2 of tens of microseconds was ascribed to solid polysaccharide in the glassy or crystalline state and showed typical Gaussian behaviour described by the equation:

$$h(t) = h_0 \exp(-t^2/2T_{2s}) \quad (14)$$

where $h(t)$ is signal intensity at time t. Below T_g these two phases are indistinguishable from the n.m.r. point of view. The second part (T_{2L}) of the decay with a T_2 of hundreds of microseconds was ascribed to the protons of water molecules of reduced mobility plus exchangeable protons of the polysaccharide and exhibited Lorentzian behaviour described by:

$$h(t) = h_0 \exp(-t/T_{2L}) \quad (15)$$

The T_2 was measured as a function of temperature (−80 to 100°C). The accuracy of the temperature measurement was ±1°C. The temperature of the sample was measured with a thermocouple. The sample was allowed to equilibrate at a given temperature for 5 min, after which the measurement was taken. The general temperature dependence of the decay is shown in *Figure 5*. At lower temperatures below T_g the T_{2s} relaxation is independent of temperature. After passing through the rigid lattice

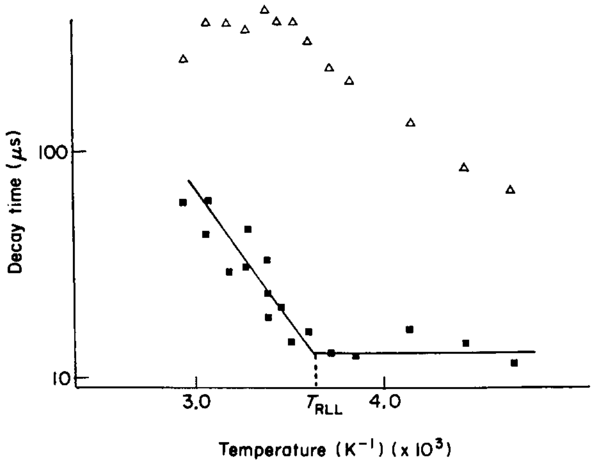

Figure 5 Typical behaviour of n.m.r. T_{2S} (■) and T_{2L} (△) as a function of inverse temperature in the region of T_g

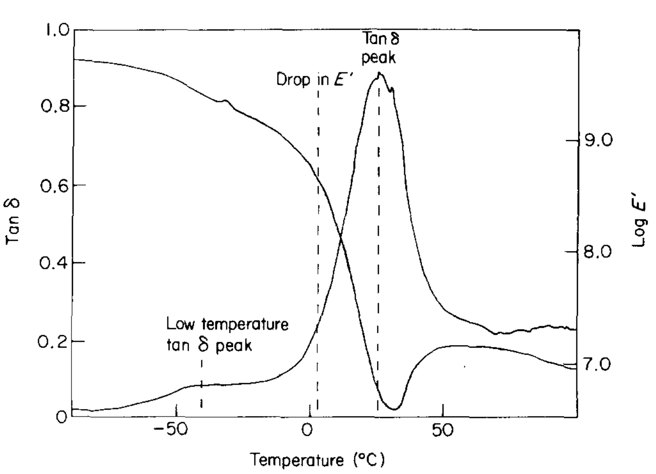

Figure 6 Typical d.m.t.a. plot for amylopectin

limit temperature (T_{RLL}) it begins to increase with temperature. This is attributed to the onset or increase in frequency of the motion of the groups containing hydrogen.

D.s.c. measurements

Calorimetric measurements were carried out as described in the previous paper[1] using a Perkin-Elmer DSC-2. The glass transition was determined from the midpoint of the heat capacity change observed at a heating rate of 10°C min^{-1}. If possible the T_g was determined from the second heating scan after cooling at 10°C min^{-1}, in order to eliminate previous differences in the thermal treatment of samples. Second runs on different samples generally had a T_g within 2–4°C of each other. The average of two to three runs was generally taken as $T_{g_{d.s.c.}}$ ($T_{g_{d.s.c.}}$ was not observed for all samples.)

D.m.t.a. measurements

The Polymer Laboratories dynamic mechanical thermal analyser mark I was used in the single cantilever bending mode at a frequency of 1 Hz and strain × 1 (corresponding to a nominal peak-to-peak displacement of 16 μm). Samples were heated at 2°C min^{-1}. Sample dimensions were typically 1.5 × 8 × 16 mm. As described in a previous paper[1] the glass transition was defined as that region between the onset of the fall in elastic modulus (E') and the peak in tan δ ($=E''/E'$, where E'' is the loss modulus), which occurs 20–50°C higher (as shown in *Figure 6*). The midpoint of the d.s.c. transition generally falls between these two temperatures.

The reproducibility of the d.m.t.a transition temperatures decreased as the transitions became broader. At low sugar contents values were generally reproducible to within 4°C. The average of runs of two to four samples was taken (it was not possible to repeat runs on the same sample due to water loss during the experiment).

Three-point bend test

An Instron texturometer and a Stable Micro Systems TA-XT2 were used interchangeably and were found to give identical results at similar rates of deformation. The TA-XT2 texture analyser was interfaced with an Amstrad PC which allowed direct determination of the gradient, peak force and storage of data on discs. The samples were similar to those used for d.m.t.a. although the length had to be > 25 mm due to the separation of the stationary supporting beams. The Young's modulus was calculated from the initial slope of force against deformation. The peak force and water content at which the sample began to snap were also recorded.

RESULTS

N.m.r. relaxation studies

These experiments were all carried out on samples prepared from native starch gelatinized in the presence of a sugar solution of appropriate concentration (i.e. the first method described above).

Amylopectin–glucose (*10:1*). Water is a very effective plasticizer as was shown previously[1]. The n.m.r. results indicate that the presence of 10% of glucose as well as water further reduces the T_{RLL} of amylopectin by an average of 25°C (*Figure 7*).

Amylopectin–glucose (*5:1*). A sample containing amylopectin and 20% glucose was prepared in the same way as previous samples. The glucose was found to be amorphous while the amylopectin displayed 2% crystallinity as shown by X-ray. This slight crystallinity was shown previously not to influence the d.s.c. or d.m.t.a. measurements but had some effect on the T_{RLL} obtained by n.m.r. When these results were compared with amylopectin–water systems where amylopectin is 2% crystalline, they showed that the effect of a further increase in the sugar concentration was not pronounced, decreasing the T_{RLL} by at most 5°C (*Figure 8*).

Amylopectin–fructose (*10:1*). An amylopectin and 10% fructose sample was examined over a wide range of temperature and moisture. The sample was 2% crystalline with respect to amylopectin as shown by a Philips X-ray diffractometer. When the T_{RLL} of this tertiary system was compared with the amylopectin–water system, T_{RLL} was substantially reduced (by 15°C) in the presence of fructose (*Figure 9*).

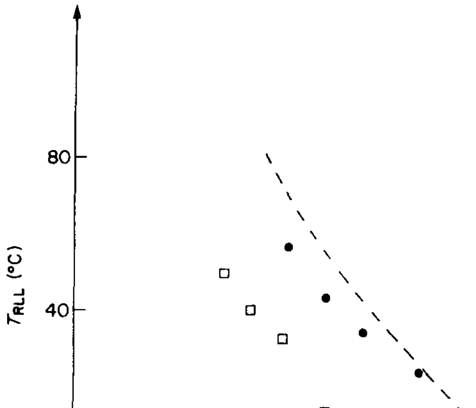

Figure 7 N.m.r. T_{RLL} (□) and d.s.c. midpoint (– – –) as a function of water content for amylopectin–glucose (10:1) compared with T_{RLL} for amorphous amylopectin (●)

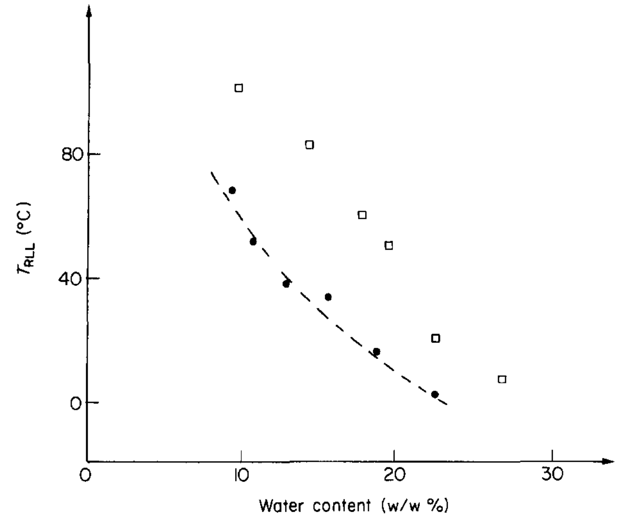

Figure 8 N.m.r. T_{RLL} (●) and d.s.c. midpoint (– – –) as a function of water content for amylopectin–glucose (5:1) compared with 2% crystalline amylopectin (□)

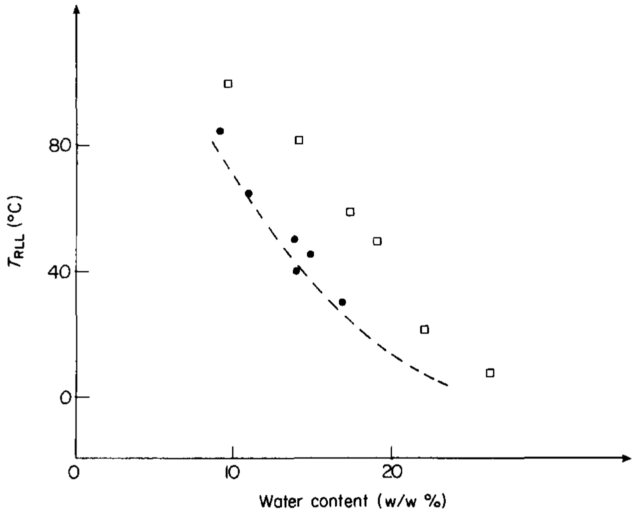

Figure 9 N.m.r. T_{RLL} (●) and d.s.c. midpoint (– – –) as a function of water content for amylopectin–fructose (10:1) compared with T_{RLL} for 2% crystalline amylopectin (□)

D.s.c. and d.m.t.a. results

There was no evidence of ice formation from the d.s.c. results and although it was not possible to carry out the d.s.c. experiments at as low temperatures as the d.m.t.a. experiments, it is unlikely that ice was formed here either as most of the samples contained <24% water, which should be unfreezable[40]. It is possible that a small amount of ice may form in the two wettest samples of amylopectin–fructose 2:1 (31.5 and 27% aqueous) although this was not seen by d.s.c. Generally these experiments were carried out on samples containing only unfreezable water.

Amylopectin–glucose (*10:1*). A sample of this composition was prepared using two different methods and compared with amylopectin containing the same weight fraction of water prepared by the same method. The results for amylopectin have been reported in a previous paper[1]. It was noted[1] that pregelatinized amylopectin (PGA) had a slightly lower T_g (4–10°C) possibly due to some residual order remaining in the samples prepared from native starch which would thereby increase the T_g. The results using samples prepared from native starch gelatinized in the presence of glucose in solution in the ratio 10:1 are plotted in *Figure 10*. The broken line indicates the position of the d.s.c. midpoint for amylopectin alone, which is ~15°C higher than the transition observed in the presence of glucose. The solid curve is the theoretical curve from this composition, which corresponds well to $T_{g_{d.s.c.}}$. The d.m.t.a. transitions show a similar drop in the glass transition in the presence of glucose—the drop in the modulus and tan δ peak occur between 11°C and 30°C lower than the same transitions for amorphous amylopectin. The greater difference is observed at low water contents as might be expected as the overall weight fraction of sugar is greater.

A similar study carried out on amylopectin from pregelatinized starch with glucose at the same composition showed a greater concentration dependence of the reduction in T_g due to the presence of the sugar (*Figure 11*). The drop in the E' temperature was 5–45°C lower and the tan δ peak 3–35°C lower than the same transition for amylopectin alone. The reduction in $T_{g_{d.s.c.}}$ was similar. These results show similar mean reduction in T_g due to the presence of glucose, but the difference in concentration dependence may be due to mixing being less thorough in the case of PGA. This is also suggested by a low temperature tan δ peak which is observed for PGA with glucose. This temperature corresponds to the glass transition of glucose at that water content. This transition was not so clearly observed for samples prepared by gelatinization of native starch in the presence of glucose solution, possibly indicating greater homogeneity in this sample (i.e. better mixing).

Amylopectin–glucose (*5:1*). These samples were prepared from native starch gelatinized in the presence of glucose solution of appropriate concentration. The d.m.t.a. results are plotted in *Figure 12*. The tan δ peak of amylopectin alone is plotted as a broken line for comparison. The reduction in tan δ peak and drop in the E' temperature due to the presence of sugar is dependent on the water content. The depression is 50–55°C at low water contents but only 14–20°C at high water contents.

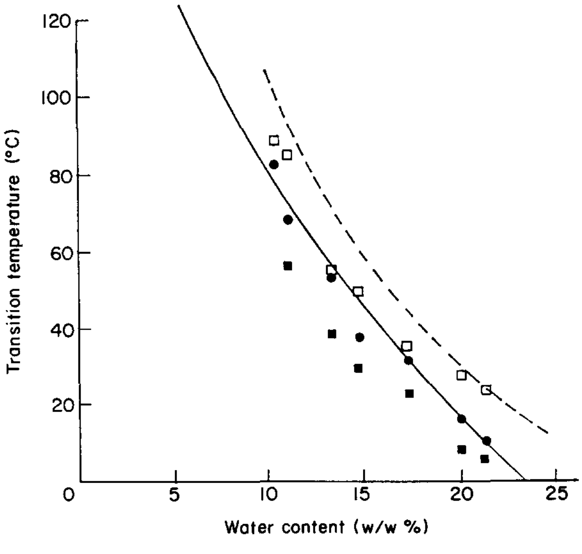

Figure 10 D.m.t.a. tan δ peak (□) and drop in E' (■) temperature and d.s.c. midpoint temperature (●) against water content for amylopectin–glucose (10:1) (prepared from native waxy maize starch). D.s.c. amylopectin alone (– – –); theoretical curve (——)

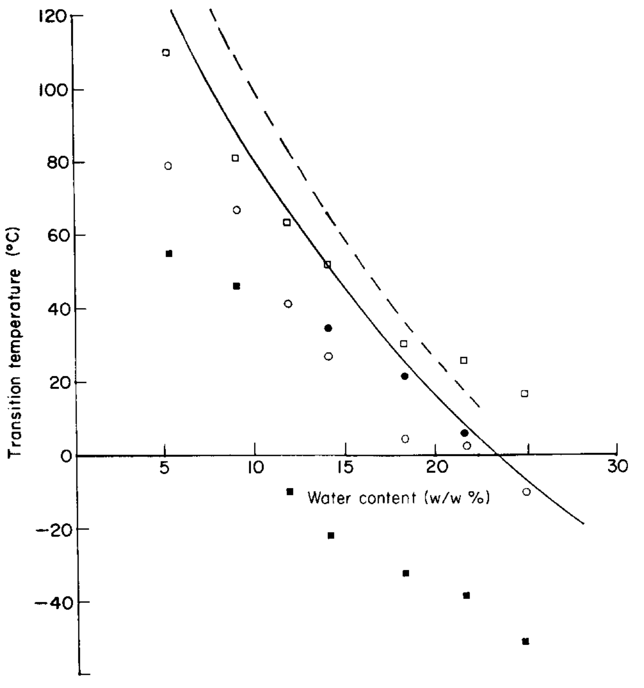

Figure 11 D.m.t.a. main tan δ peak (□), low temperature tan δ peak (■), drop in E' (●) and d.s.c. midpoint (○) for pregelatinized waxy maize starch–glucose (10:1) pressed at 95°C. D.s.c. amylopectin alone (– – –); theoretical curve (——)

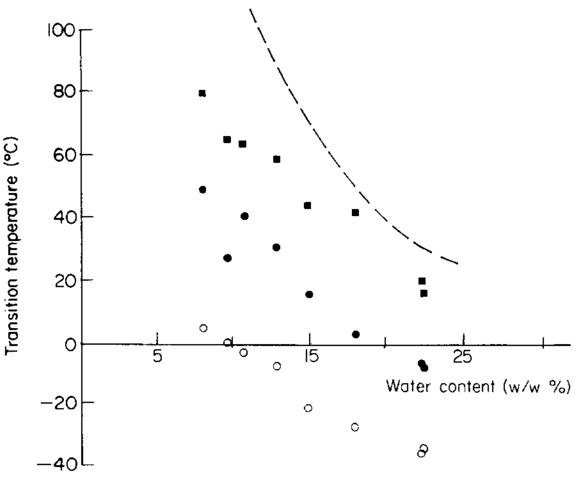

Figure 12 D.m.t.a. main tan δ peak (■), low temperature tan δ peak (○) and drop in E' (●) for amylopectin–glucose (5:1). Tan δ peak for amylopectin alone (– – –)

The depression of the onset of the drop in E' is greater than the depression of the tan δ peak—this results in a broader transition. The d.s.c. results shown in *Figure 13* also show an increased drop in T_g with an increase in glucose content. The d.s.c. results of amylopectin alone are plotted as a broken line for comparison, and the theoretical curve for this glucose content is plotted as a smooth line.

As pointed out for the n.m.r. results, this sample was found to have 2% crystallinity in amylopectin (none in sugar). There was no need to take this into account in analysing the d.m.t.a. and d.s.c. results as 2% crystallinity was found to have no significant effect, as far as d.m.t.a. or d.s.c. was concerned[1]. However, crystallinity may contribute to the breadth of the transition in the presence of sugar. The height of the tan δ peak for this system (0.32 average) was slightly lower than for amylopectin (0.39), whereas for the previous sample (amylopectin–glucose 10:1) it was higher (0.58) than for amylopectin alone. The height of the tan δ peak corresponds to the fraction of the sample undergoing the transition[41], therefore a reduction in the height of the tan δ peak in this system indicates greater sample heterogeneity. This was further evidenced by a clear tan δ peak observed at low temperatures corresponding to the glucose T_g (as observed previously for PGA–glucose 10:1). It is apparent that increasing the glucose content results in an increased depression of the T_g relative to that of amylopectin alone. The effect of different sugars was also studied.

Amylopectin–fructose (10:1). This sample was prepared by the first method (from native starch and sugar solution). X-ray diffraction showed the small degree of crystallinity in the amylopectin (2%) and none in the fructose. As stated above this is not expected to affect d.s.c. and d.m.t.a. results. The d.m.t.a. results plotted in *Figure 14* show a drop (12–38°C) in both transitions when compared with amylopectin alone, which is greater than the decrease in T_g observed for amylopectin–glucose (10:1) and not as great as the decrease observed for amylopectin–glucose (5:1). The average height of the tan δ peak is similar to that for amylopectin–glucose (10:1).

Amylopectin–sucrose (10:1). This sample was prepared from pregelatinized starch by the liquid nitrogen method, followed by pressing at 90°C. There was no evidence of starch or sugar crystallinity by X-ray. The results are plotted in *Figure 15*. As for the previous samples there was a reduction of all transition temperatures when compared with amylopectin of the same water content. The reduction was greatest at low water contents and greater for d.s.c. (10–43°C) and the drop in E' (2–31°C) than for the tan δ peak (0–10°C) indicating broadening of the transition. This decrease was also observed for the other sugars, particularly at higher water contents.

Amylopectin–xylose (10:1). This sample was prepared from PGA by hot pressing in the usual way. This system was of special interest since xylose has been found to

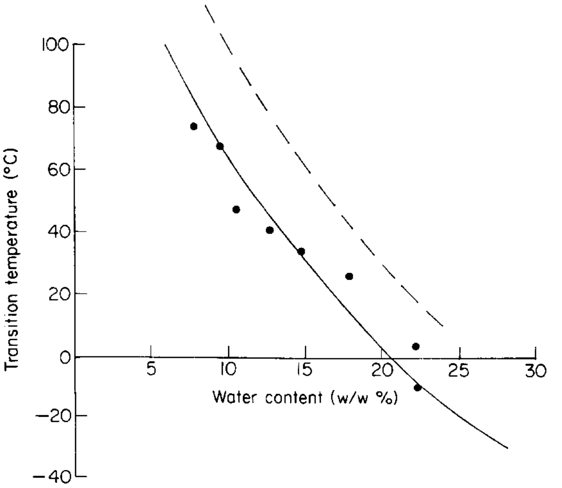

Figure 13 D.s.c. midpoint temperature for amylopectin–glucose (5:1) (●). $T_{\mathrm{gd.s.c.}}$ amylopectin alone (– – –); theoretical curve (——)

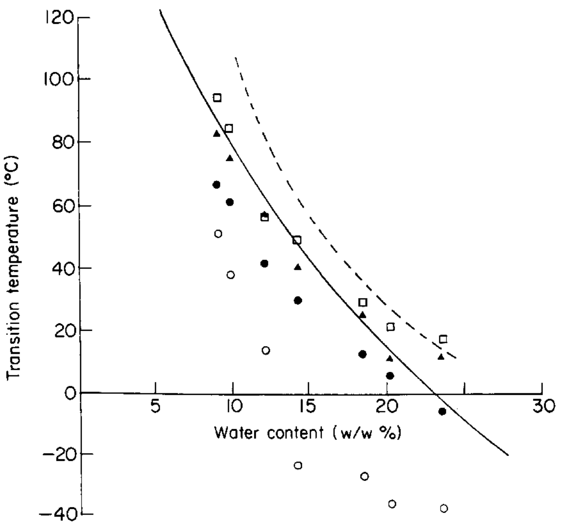

Figure 14 D.s.c. midpoint temperature (▲) and d.m.t.a. tan δ peak (□), low temperature tan δ peak (○) and drop in modulus (●) temperature for amylopectin–fructose (10:1). D.s.c. midpoint for amylopectin alone (– – –); theoretical curve (——)

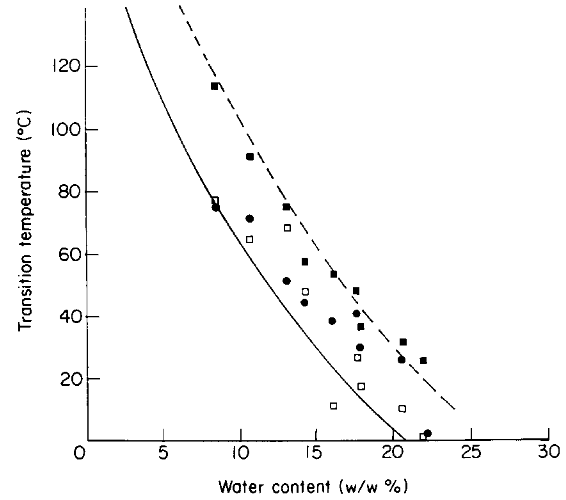

Figure 15 $T_{\mathrm{gd.s.c.}}$ (●) and d.m.t.a. tan δ peak (■) and drop in modulus (□) temperature for amylopectin–sucrose (10:1). Theoretical d.s.c. curve for amylopectin alone (– – –); theoretical d.s.c. value for this system (——)

have a greater inhibiting effect on the recrystallization of starch than glucose, maltose or even maltotriose[42]. It has been argued that sugars may have an antiplasticizing effect (increasing T_g) and that this might be an explanation for these results.

The d.s.c. results for this system are plotted in *Figure 16*. The theoretical line is plotted with the data and gives a good fit, as for the other amylopectin–sugar mixtures i.e. the presence of xylose has resulted in a 10–25°C drop in T_g. At intermediate water contents (13–24%) the first and second run by d.s.c. give very similar T_g values. At low water contents there may be some problems due to water loss above T_g which is not readsorbed by the sample in time for the second run, thus the two driest samples give a much higher T_g on the second run. The transition also becomes broader and more difficult to analyse for the drier samples. In this case the T_g value obtained on the first run appears to fall on the theoretical curve.

The d.m.t.a. results are plotted in *Figure 17*, with the theoretical curve for the mixture plotted for comparison. As well as a drop in modulus and tan δ peak falling on either side of the d.s.c. transition, there is also some evidence of a low temperature transition in the region of the T_g of xylose at that water content. When compared with the d.m.t.a. results for amylopectin, the presence of xylose has broadened the transition with the drop in modulus temperature falling more than the tan δ peak temperature. The change is particularly great at low water contents, as observed for the other samples.

Amylopectin–fructose (*2:1*). An attempt was made to study a system with a larger proportion of sugar. Fructose

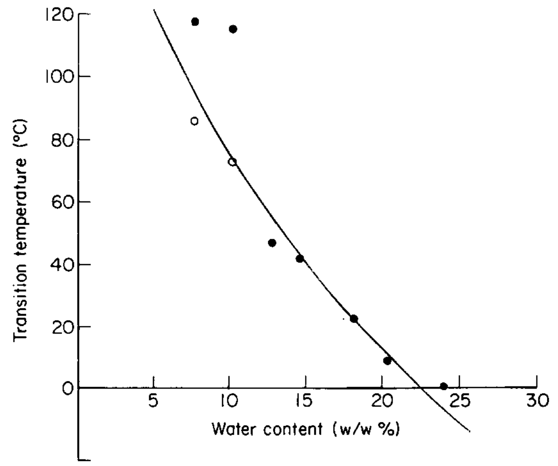

Figure 16 Amylopectin–xylose (10:1) d.s.c. results: run 1 (○); run 2 (●). The curve is the theoretical curve obtained using method 1

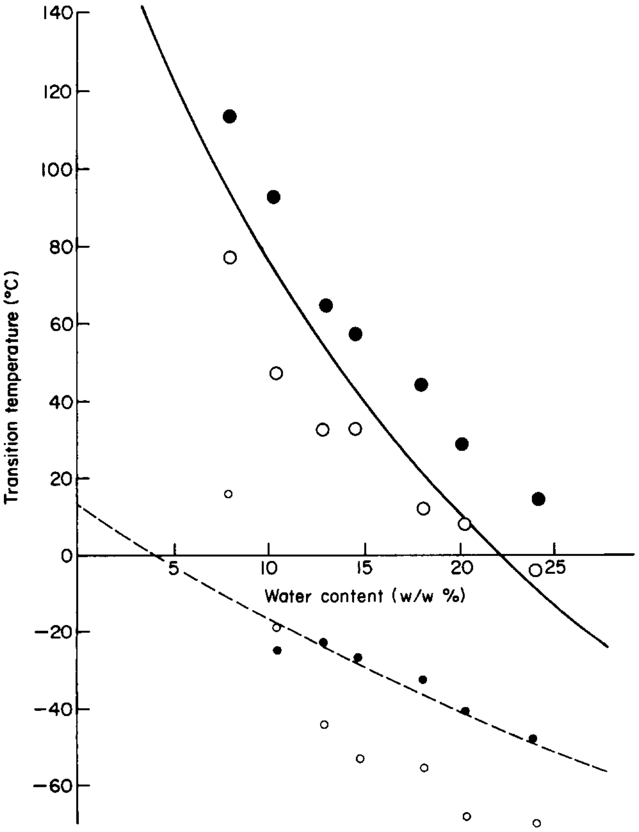

Figure 17 Amylopectin–xylose (10:1) d.m.t.a. results: major tan δ peak (●); minor tan δ peak (•); high temperature drop in E' (○); low temperature drop in E' (o) and calculated $T_{\mathrm{gd.s.c.}}$ of xylose (– – –)

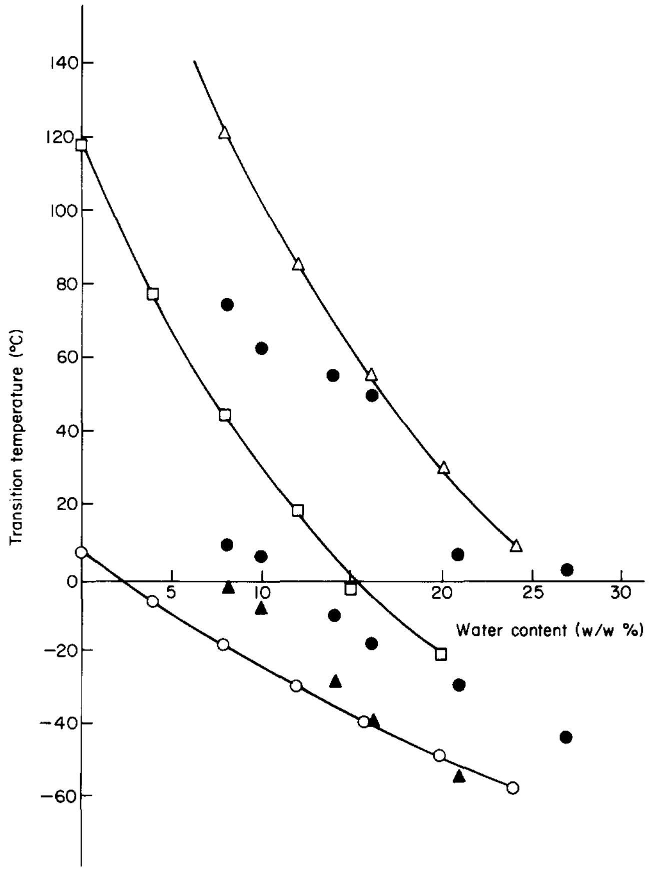

Figure 18 D.m.t.a. tan δ peaks (●) and drop in modulus (▲) temperatures for amylopectin–fructose (2:1). Theoretical d.s.c. curve for amylopectin alone (△); theoretical d.s.c. curve for amylopectin–fructose (2:1) (□) and theoretical d.s.c. curve for fructose alone (○)

was chosen as it was found to have the greatest plasticizing effect and was thought to be least likely to crystallize. There was no transition observable by d.s.c. The d.m.t.a. results are plotted in *Figure 18*. Again two tan δ peaks are generally observed, the first corresponding to the fructose-rich phase and the second to the amylopectin-rich phase. The peaks are of similar heights depending on the water content. At low water contents, the high temperature peak appears to dominate and at higher water contents the low temperature peak may be the larger. The main drop in the modulus occurs below the first peak but at lower water contents a higher temperature drop in modulus is also observed. This is shown by the d.m.t.a. plots at r.h. 85% (21% aqueous) and r.h. 43% (10% aqueous) (*Figures 19a* and *b*, respectively).

The higher tan δ peak temperature shows 15–44°C depression when compared with results for amylopectin alone. The drop in modulus temperature corresponds very closely to the fructose $T_{\mathrm{g_{d.s.c.}}}$ curve. As the drop in the modulus normally occurs 10–20°C below T_g by d.s.c., this indicates that the drop in modulus corresponds either to fructose of reduced water content or fructose with an increased T_g due to the presence of amylopectin. In general this appears to be a multiphase system with some interaction of the two components. There was also a small amount of crystallinity in the starch (up to 5%), especially at higher water contents, due to retrogradation, which may add to difficulties in interpretation.

Three-point bend test

All tests were performed on samples prepared using PGA by hot pressing under pressure above T_g, as it was very difficult to obtain sufficiently long flat samples by the other method. Amylopectin alone is plotted with amylopectin–glucose data in *Figure 20*. The arrows indicate the approximate water content at which the samples snap rather than just yield. It is obvious that sugars decrease the modulus of amylopectin, and decrease the water content at which the sample snaps, reducing the T_g or water content. Within the range of water contents studied, amylopectin–glucose (5:1) and (10:1) appeared to begin to snap at a very similar water content (~14%). The modulus clearly rises steeply in the case of amylopectin–glucose (5:1) at a lower water content than (10:1) indicating the increasing plasticizing effect of the sugar. At high water contents their moduli are more similar, perhaps because the glucose viscosity is increasing as its glass transition is approached within 30–40°C.

Figure 21 shows three-point bend test results for amylopectin compared with amylopectin–fructose (2:1) and amylopectin–sucrose (10:1). The logarithm of the modulus of amylopectin–sucrose (10:1) is very similar to that of the amylopectin–glucose (10:1), becoming a little higher at low water contents (<14%) probably due to the higher T_g of sucrose. As expected the modulus of amylopectin–fructose (2:1) is much lower than other samples at low water contents (<15%), but it does not decrease as rapidly as might be expected. This may be due to some reordering of amylopectin occurring at

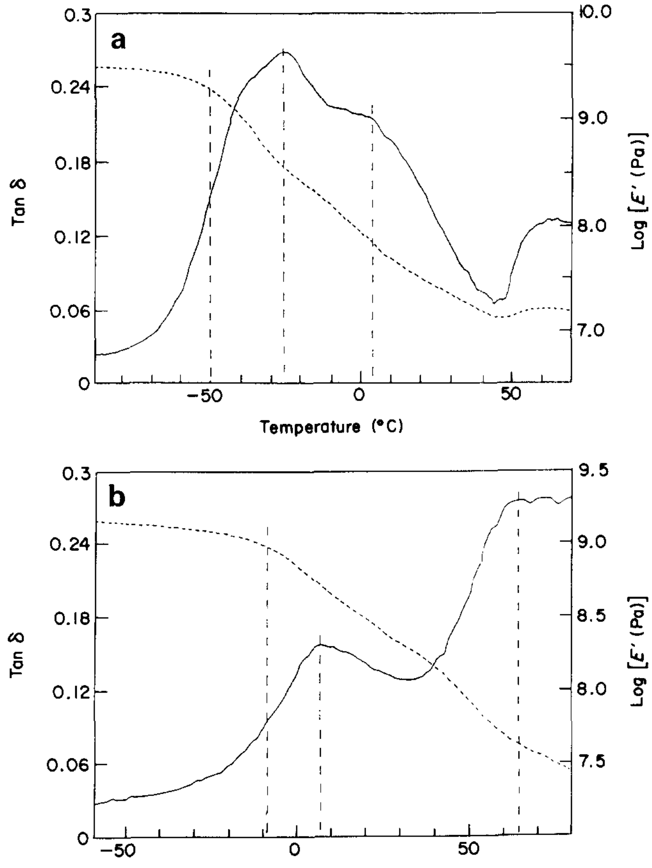

Figure 19 D.m.t.a. tan δ (—) and log E' (- - -) plots for amylopectin–fructose (2:1): (a) r.h. 85%; (b) r.h. 43%

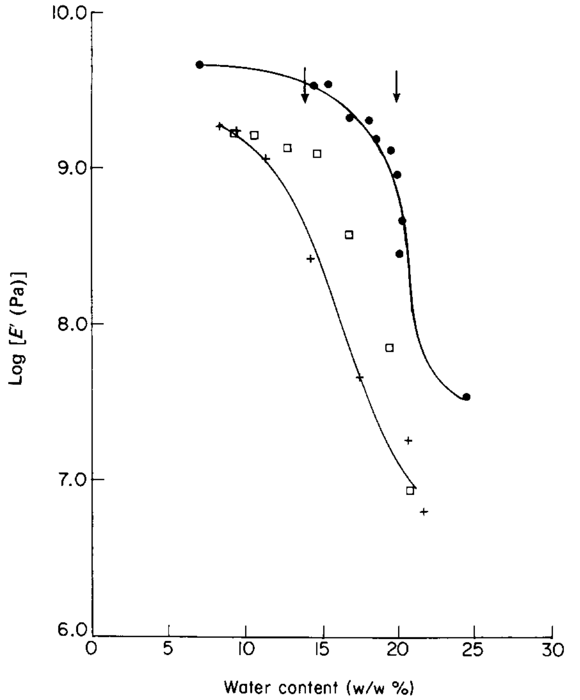

Figure 20 Three-point bend test results for amylopectin (●) and amylopectin–glucose (10:1) (□) and (5:1) (+)

higher water contents (the sample was found to contain 2–8% crystallinity in amylopectin, with some dependence on r.h.). The onset of snapping also occurred at a somewhat lower water content than for other samples, i.e. at <12% aqueous.

DISCUSSION

Comparison of results from different techniques

Similar trends are observed as were found in the previous paper on amylopectin alone[1]. The d.s.c. mid-point generally occurs between the tan δ peak and drop in modulus by d.m.t.a. The n.m.r. transition occurs 5–35°C below the d.s.c. transition. In the presence of sugars the situation is somewhat confused as a small amount of crystallinity in the starch appears to have a large effect on T_{RLL} (an increase of 10–40°C in T_{RLL} was observed for crystallinity of 2–4%). This makes the n.m.r. results more difficult to interpret although, if sugar–amylopectin samples containing partially crystalline amylopectin are compared with amylopectin of a similar crystallinity, sugars are found to have a plasticizing effect by n.m.r. as also observed by d.m.t.a. and d.s.c.

The effect of crystallinity also has an interesting effect on comparison with the d.s.c. results. As the presence of 2% crystallinity greatly increases T_{RLL}, for the slightly crystalline samples T_{RLL} actually equals $T_{g_{d.s.c.}}$, instead of being 5–35°C below the d.s.c. transition (see *Figures 8* and *9*). The increased T_g depression observed for the ratio 5:1 amylopectin–sugars by d.m.t.a. and d.s.c. as against 10:1 is not observed by n.m.r. It appears that, as in the case of crystallinity, a small amount of sugar has a significant effect on T_{RLL}, but subsequent increases in the sugar content have a reduced effect. The explanation for this is not entirely clear, except that n.m.r. is looking at changes occurring at a molecular level, whereas d.m.t.a. and d.s.c. are sensitive to macroscopic changes occurring as a result of changes on the molecular level. The difference in the nature of the techniques would be expected to give some different results. (The effect of frequency on these samples was discussed in a previous paper[1]).

Effect of sugar type and content

The d.m.t.a. and d.s.c. results show a clear difference in the effect of different sugars and their concentrations. The degree of plasticization by sugars appears to increase in the order: sucrose < glucose < xylose < fructose. Sucrose is a disaccharide and has a higher molecular weight than glucose, xylose or fructose and not surprisingly has a higher T_g (70°C)[19] and thus is expected to have a reduced plasticizing effect when compared with the other sugars. Glucose and fructose have the same molecular weight (180) but fructose has a lower T_g (7°C as against 38°C for glucose), and therefore fructose is expected to have a greater plasticizing effect. Xylose has the lowest molecular weight (150), but has a slightly higher T_g than fructose (13°C). The $T_{g_{d.s.c.}}$ for amylopectin–xylose (10:1) appears to fall between that for samples containing fructose and glucose at the same ratio. The broadening of the d.m.t.a. transition makes comparison of the data more difficult. The plasticizing behaviour of xylose indicates that the T_g value and not the molecular weight is the most important factor in determining plasticization. Adding an increased weight fraction of glucose further reduced $T_{g_{d.s.c.}}$ by 15°C.

Our results for amylopectin–xylose (10:1) indicate that xylose does not have an antiplasticizing effect on the amylopectin glass transition, as has been suggested[42] to explain the decreased rate of retrogradation of starch and increased gelatinization temperature in the presence of xylose. These results are generally obtained at a starch–water ratio of 1:1, which results in a predicted T_g (by the Couchman–Karasz equation) below −70°C or at ~−40°C when sugar is added in the ratio 1:1:1 (starch–sugar–water). (This increase in T_g is due to the

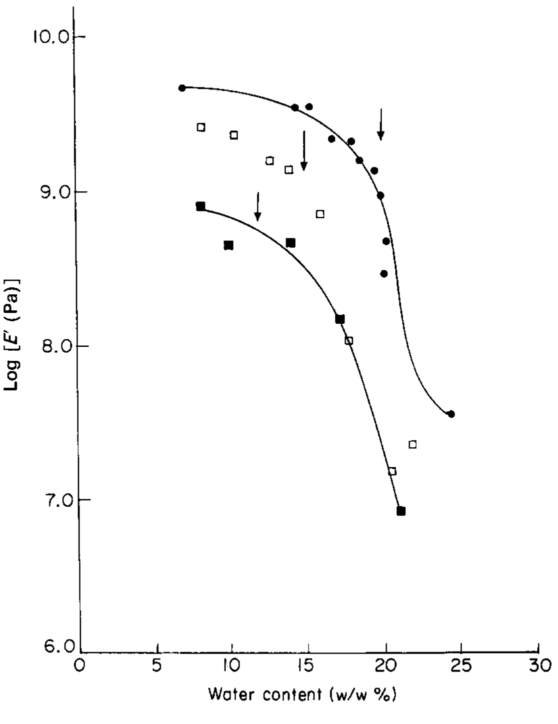

Figure 21 Three-point bend test results for amylopectin (●) and amylopectin–sucrose (10:1) (□) and amylopectin–fructose (2:1) (■)

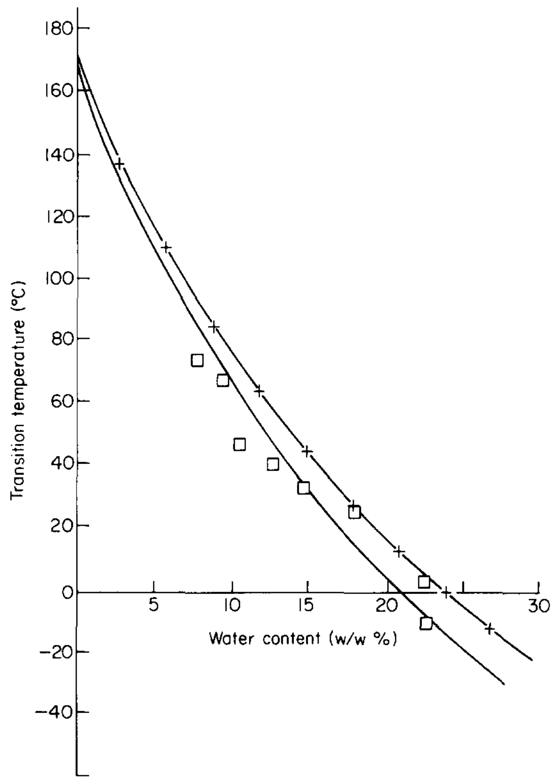

Figure 22 $T_{g_{d.s.c.}}$ for amylopectin–glucose (5:1) (□) compared with theoretical curves obtained using method 1 (——) and method 2 (– + –) (see text)

decreased weight fraction of water.) Retrogradation studies, generally carried out at or above room temperature, are not likely to be controlled by a T_g more than 60°C below. Even if the T_g does have some influence, the predicted differences between the sugars are not observed in practice.

The inhibiting effect of xylose on starch retrogradation relative to fructose[42,43], glucose or sucrose[42] is not explained by its effect on T_g. The rate of retrogradation has been found to decrease in the order: fructose > glucose > sucrose > xylose[42]. Apart from xylose, these are in the order of increasing T_g. Our results have shown that there is nothing anomalous about the T_g behaviour of xylose in the presence of amylopectin. Other factors such as viscosity and the water structuring effect of sugars also have an important influence on the retrogradation rate and gelatinization temperature of starch.

A sample prepared from amylopectin–fructose (2:1) showed a substantial influence of the sugar T_g on the modulus (d.m.t.a., *Figure 18*). The onset of the drop in modulus occurred close to the sugar T_g. This appears to be a multiphase system with some plasticization of the main $\tan\delta$ peak, but not as much as might be expected for such a large sugar content.

Comparison of data with theoretical equations

The Couchman–Karasz equation two-component (method 1) approach described earlier was found to give a better fit to the data for starch–sugar mixtures than method 2. This is evident in *Figure 22* where the d.s.c. data for amylopectin–glucose (5:1) are plotted with the two theoretical curves. Method 1 predicts greater plasticization as the ΔC_p of the sugar (which is higher than that of starch) is not taken into account. It is assumed that ΔC_p of sugar and starch is the same as that for starch alone. This may be correct when the sugar content is low.

The two-component approach was found to give reasonable agreement with experiment for all amylopectin sugar mixtures studied at low sugar contents. The amylopectin–fructose (10:1) data fall below the calculated curve at low water contents and above it at higher water contents. This is observed more strongly in the case of amylopectin–sucrose (10:1) where the results fall between the two theoretical curves. The theoretical curves do predict less difference between starch, and starch and sugar at high water contents, due to the smaller weight fraction of sugar, but not as great a difference as is observed in practice [except possibly in the case of amylopectin–glucose (10:1)]. This trend is also observed for the d.m.t.a. results and may be due to phase separation which is predicted to flatten out T_g composition dependence[18,28]. This may be enhanced in the case of sucrose due to its higher molecular weight. Ten Brinke *et al.*[18] also predict a greater than normal change in T_g with plasticizer if specific interactions between polymer and solvent are present. Thus a possible explanation for the success of the two-component equation instead of the three-component equation (which predicts a lower plasticizing effect of water), is that at low water contents there may be amylopectin–sugar interactions, which are replaced by amylopectin–water and sugar–water interactions at higher water contents. However, it is not straightforward to apply equations which take account of interactions to three-component systems, especially when it is difficult to prepare perfectly homogeneous samples. These equations were not applicable to amylopectin–water, so it would be unlikely for them to be applicable to amylopectin–sugar mixtures in the presence of water.

It appears that the samples containing pregelatinized starch, prepared at low water contents may be less homogeneous than those prepared at 50% water. For example, in the case of amylopectin–glucose (10:1) a d.s.c. transition was more difficult to see and a low temperature transition (corresponding to the sugar T_g) was more clearly observed by d.m.t.a. for a sample prepared at lower water contents.

The results for a sample containing a high sugar content, amylopectin–fructose (2:1) are interesting to compare with theoretical plots. Unfortunately no clear d.s.c. transition was observed. The mechanical behaviour seems to be dominated by the presence of fructose with the modulus beginning to fall at a somewhat higher temperature than would be expected for fructose alone (at d.s.c. midpoint). A low temperature $\tan\delta$ peak behaves in a similar way, whereas the high temperature $\tan\delta$ peak is 14–18°C below that for amylopectin alone, but 30–40°C above the value predicted for a homogeneously miscible system (*Figure 18*). Thus it appears that this is a multiphase system, the dominant components being a fructose-rich phase (containing some amylopectin) and an amylopectin-rich phase (somewhat plasticized by fructose). The two $\tan\delta$ peaks are often not well defined, so in fact there may be a range of compositions between these two major ones. It is quite probable that a different sample preparation method may allow the phases to separate more clearly, or alternatively it may be possible to obtain a single phase composition.

The Couchman–Karasz equation therefore gives a good first approximation of the T_g of these systems.

Divergence may be due to phase separation, starch crystallinity or specific interactions, which in turn depend on sample preparation and composition.

CONCLUSIONS

In general, we have shown that sugars have a plasticizing effect on starch, reducing T_g and Young's modulus. At low sugar contents ($<20\%$ relative to starch) there seems to be miscibility and a behaviour in the presence of water that can be adequately modelled by a Couchman–Karasz equation. At higher sugar contents, and possibly at higher water contents, the transition is broadened and in the case of amylopectin–fructose (2:1), there appears to be a multiphase system containing amylopectin-rich and fructose-rich regions. The nature of such samples is expected to be especially sensitive to the sample preparation method and thermal history. These results indicate that the effects of sugars in reducing retrogradation of starch and increasing the gelatinization temperature are not due to their effect on T_g but due to more specific effects.

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NOTE ADDED IN PROOF

We have recently been made aware of a publication by Hallbrucker *et al.* (*J. Phys. Chem.* 1989, **93**, 4986) reporting substantially smaller values of the ΔC_p at T_g of water than those used here. The significance of this to our use of the Couchman–Karasz equation is discussed in a paper published in the *International Journal of Biological Macromolecules* (1992, **14**, 257).